

Structural and photocatalytic properties of TiO₂ films fabricated on silicon substrates by MOCVD method

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Abstract: Silicon(111) and Silicon(100) were employed for fabrication of TiO₂ films by metal organic chemical vapor deposition(MOCVD). Titanium(IV) isopropoxide(Ti[O(C₃H₇)₃]) was used as a precursor. The as-deposited TiO₂ films were characterized with FE-SEM, XRD and AFM. The photocatalytic properties were investigated by decomposition of aqueous Orange II. And UV-VIS photospectrometer was used for checking the absorption characteristics and photocatalytic degradation activity. The crystalline and structural properties of TiO₂ film had crucial influences on the photodegradation efficiency. For MOCVD *in-situ* deposited films on Si substrates, the photoactivities varied following a shape of "M": at lower(350°C), middle(500°C) and higher(800°C) temperature of deposition, relative lower photodegradation activities were observed. At 400°C and 700°C of deposition, relative higher efficiencies of degradation were obtained, because one predominant crystallite orientation could be obtained as deposition at the temperature of two levels, especially a single anatase crystalline TiO₂ film could be obtained at 700°C.

Keywords: MOCVD; photocatalytic degradation; Silicon(100); Silicon(111)

Introduction

Titanium oxide is an *n*-type semiconductor with many interesting properties. It is transparent to visible light, has high refractive index, nontoxic, low absorption, high dielectric constant and chemical stable. Indeed titanium dioxide has been extensively investigated for many marvelous applications, such as photocatalytic detoxification of polluted water and so on(Lisenbigler, 1995). The photocatalysis of TiO₂ has been investigated extensively for the advantages of its remarkable activity, low cost, chemical and radiation stability-not prone to photocorrosion(Mills, 1993).

Orange II is a textile azo-dye, which resistant to light degradation, and not easy to react with O₂, common acids and bases. Further more, Orange II does not undergo biological degradation in wastewater treatment plants. In anaerobic conditions, it can be reduced to potentially carcinogenic aromatic amine(Halmann, 1996). For removing this recalcitrant organics, traditional methods like ultra-filtration, extraction, air stripping and carbon adsorption and so on are non-destructive; only simply transfer pollutant from one phase to another(Dhananjay, 2001). TiO₂ photocatalysis may be the best alternative for azo-dye degradation, because at first, this process involves the destruction of organic contaminants rather than transfer them from one phase to another. Secondly, utilization of this process has great potential as it operates near ambient temperature and pressure, and solar light can be used as illuminating source(Mills, 1997).

Up to now much attention have been paid on the using of fine or ultrafine TiO₂ photocatalytic powders in a slurry state, because higher efficiencies can achieve by increasing

effective surface areas. However, the use of aqueous suspensions limits practical applications for problems of separation of fine particles of TiO₂ and the recycling of the photocatalysts(Anita, 2002). There are many methods for making immobilized TiO₂. Metal-organic chemical vapor deposition(MOCVD) technique has been widely applied for the preparation TiO₂ films because of its many advantages(Kang, 2000).

Recently several studies have focused on the influence of different crystallitic structure on photocatalytic activity. The photocatalytic efficiency of TiO₂ is governed by its crystal structure. There exist considerable differences in photocatalytic degradation activity because of different crystallite orientation, even with the same phase of anatase(Tsai, 1997). But to our knowledge there are few systemic studies on the relationship between crystal structure and photocatalytic activities especially for that of TiO₂ films produced through MOCVD. Based on the previous investigations on crystallite properties of TiO₂ films, it seemed that there were some controversies about TiO₂ growth behavior, such as phase transforming temperature and the type of predominant orientation and so on(Djaoued, 2002; Gnanasekar, 2002). Thus carrying out researches on the crystal properties and its influence on photocatalytic activities are necessary and essential.

The purpose of this research is systematically investigating the influence of TiO₂ films fabricated at different conditions on crystallization characteristics and photocatalytic activity. In this study, TiO₂ film was deposited on silicon substrates using MOCVD technique. The as-deposited films were used to check crystallite properties, photoactivities for degradation dye solution(Orange II). Some important

conclusions have been obtained and discussed. Reasons that caused some unusual performances have also been analyzed.

1 Experimental description

1.1 TiO₂ films deposited by MOCVD process

Deposition of TiO₂ thin films was carried out in a homemade low-pressure vertical metal organic chemical vapor deposition(MOCVD) system. Inside the quartz chamber the substrate was mounted on a SiN covered graphite susceptor which was heated by a 1 kW induction coil heater, the susceptor temperature can be controlled automatically from 300°C to 1100°C. TIP-titanium iso-propoxide (Ti [OCH(CH₃)₂]₄) had been used as a single molecular precursor. Argon gas with purity of 99.999% was employed as carrier and diluting gases, oxygen of 99.999% was used to supply oxidative atmosphere for precursor. The general deposition conditions are as follows: temperature ranged from 300°C to 800°C; pressure ranged from 0.1 to 5 torr; the flow rate of diluting gas, TIP carrier gas and O₂ was 10—40 scc/min, 10—40 scc/min and 20 scc/min, respectively.

Silicon substrates were cut as 13 mm × 20 mm. Before mounted onto graphite susceptor, each substrate was cleaned in a sonicator with acetone followed by methanol for about 4 min respectively for degreasing, then rinsed in deionized water and at last it was immersed into 10% (wt%) HF solution for about 1 min to dissolve the very thin layer of SiO₂.

1.2 Checking microstructural, crystal and other TiO₂ film properties

The crystal structure of as-deposited specimen were examined by X-ray diffraction(XRD), a high quality XG, M18XCE diffractometer(MAC Science Co. Ltd.) using Cu K α ($\lambda = 1.54056\text{\AA}$) radiation at 40 kV and 200 mA, scanning rate was 8°/min. The surface morphology and cross-sections of films were observed by using a field emission scanning electron microscopy (FE-SEM). This PHILIPS XL30SFEG FE-SEM has resolution of 1.5 nm at 10 kV or higher and 2.5 nm at 1 kV, beam current range from 1 pA to 20 nA, magnification range(related to image width of 12 cm) from 20 to 800000, and it was fixed with energy dispersion system(EDS) analysis system(sapphire detectors with EAP + crystal). The higher resolution of this SEM system makes possible for getting high quality images of films.

An autoprobe atomic force microscope AFM was introduced to study the surface topography of amorphous and polycrystalline TiO₂ films.

1.3 Checking the photocatalytic activity of TiO₂ films

As-deposited TiO₂ films were immersed into 6.5 ml, 0.01 mmol/L dye solution of Orange II (HOC₁₀H₆N = C₆H₄SO₃Na, dye content 85%, products of Aldrich Chemical Company, Inc.). This aqueous solution with pH = 6.2 was put into a cylindrical transparent polymeric container

with diameter and height of 30 mm and 5 mm respectively. The solution container was located in a homemade chamber equipped with 200 W mercury lamp that can produce UV and visible light that irradiated on TiO₂ films through a Pyrex filter cover. The light intensity on films can be adjusted by changing the distance between UV-lamp and sample supporting plate. The light intensity was measured with a power meter(Newport 1815-c). In this experiment, the intensity of light was controlled to 5.5 mW/cm². All of the experiments were carried out at ambient temperature (25—40°C) and pressure.

After certain period of irradiation the sample of dyed Orange II solutions were sent for checking the degradation (decolorization) so as to measure the photocatalytic activity of TiO₂ films. The photocatalytic degradation analytic system was 2401PC UV-VIS recording spectrophotometer (SHIMADZU) with scanning wave ranged from 200 nm to 800 nm. The volume of solution container used for scanning in UV-VIS 2401PC spectrophotometer was 0.74 ml. The visible light of 486 nm wavelength was employed for checking the dye decolorization. The diagram of relationships between absorbance and wavelength would be plotted automatically after finishing the scanning of a sample of dye solution.

2 Results and discussion

2.1 TiO₂ thin films fabricated within 30 min on Si (100) substrates and illuminated by UV-light

TiO₂ thin films were deposited on Si(100) wafers at a temperature range from 360°C to 900°C within 30 min. OSA 36, OSA 40, OSA 43, OSA 46, OSA 50, OSA 60, OSA 70, OSA 80 and OSA 90, corresponded to the deposition temperature of 360, 400, 430, 460, 500, 600, 700, 800 and 900°C respectively. All of the depositing operation parameters were kept unchanging except varying the deposition temperature. The thickness of films was 200—400 nm. The as-grown films were immersed in 6.5 ml, 0.01 mmol/L Orange II solution and irradiated by UV-light (5.5 mW/cm²) for 2 h.

Fig.1 shows the results of UV-VIS spectra. Fig.2 shows the relationship between dye concentration variation and thin films synthesized temperatures. These two figures showed that the film fabricating temperature had shown crucial influence on characteristics of photodegradation. As deposition temperature changed from 360°C to 900°C, the proportion of dye conversion displayed a "M" shape with somewhat lower on left shoulder. The two shoulders were located on the vicinity of 430°C and 700°C. At middle range the lowest position was observed near 500°C. At relative low and high temperature the values of degrading proportion were also very small. It seems to be unbelievable and easily confused. So discussing the reasons causing this phenomenon is necessary and essential. The possible explanation is given as follows.

It is well believed that the crystallization is essential for

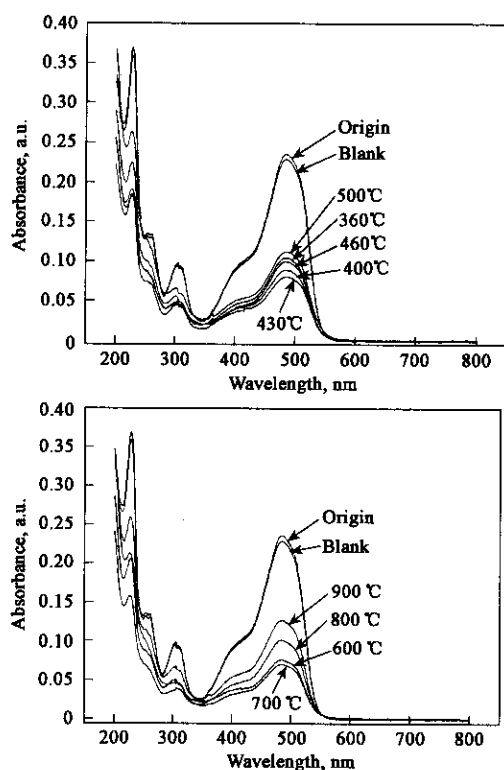


Fig. 1 UV-VIS scanning spectra of dye solution photo-degraded by TiO_2 thin films with thickness of 200–400 nm deposited at different temperatures ranged from 360°C to 900°C

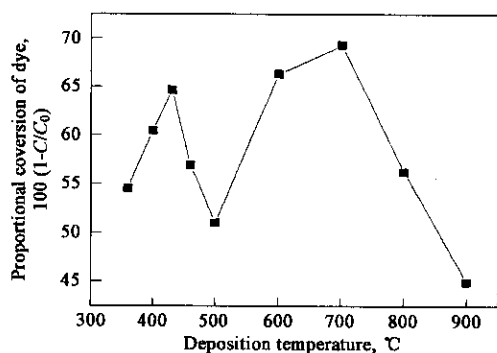


Fig. 2 The influence of TiO_2 thin film depositing temperature on activities of photocatalytic degradation

maintaining TiO_2 photocatalyst in a high level of degradation ability (Jang, 2001; Rivera, 1993). So at first let's take a look at the XRD patterns shown in Fig. 3, at relative lower temperature (360°C) of TiO_2 film deposition, the crystallization did not fully developed, so it was reasonable for getting a lower activity of photodegradation. At 430°C the intensity of anatase (101) attained a highest level among the other displayed results. That means the crystallization was improved, so the photocatalytic degradation would be accelerated, thus appeared the left shoulder of "M" in Fig. 2. At 500°C, there were even no anatase crystallite peaks can be observed, that indicated some structural changing had already taken place. During this process, the film crystal structure changed to some other orientations,

corresponded with the decreasing of crystallite size. As literature elucidated that increasing crystallite size would benefit for improving the degradation of aqueous organic compound. At 600°C and 700°C the new predominant orientation of A(112) appeared. The anatase of A(112) tends to form well standing micro-scale columns as shown in Fig. 4. This would improve the kinetic conditions of degradation reaction at the interfacial area between liquid dye and solid columns. At 700°C, the anatase A(112) peak was enhanced further more. And on the other hand the calculated crystallite size attained the largest among all of the adopted samples (the calculated crystalline size of 360°C, 430°C, 500°C, 600°C, 700°C and 800°C deposition is 43.1 nm, 46.2 nm, 35.4 nm, 56.5 nm, 58.8 nm and 55.0 nm respectively). Thus it was reasonable to believe that the photoactivity of films deposited at 700°C would be the highest one. From 700°C to 800°C the calculated crystallite size decreased and anatase (101) appeared again. The polycrystallization and small crystalline of TiO_2 film would result in the decrement of photodegradation efficiency. At 900°C the crystallite size (49.4 nm) decreased further, so the photocatalytic activity decreased correspondingly.

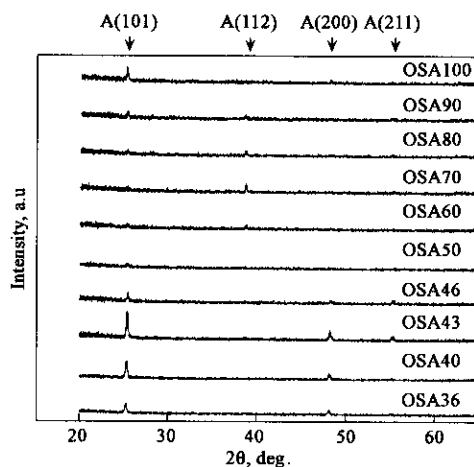


Fig. 3 The XRD patterns of TiO_2 films growing at different temperature on different Si(100) substrates within 30 min for each individual deposition

Fig. 4 shows the FE-SEM images of TiO_2 thin films synthesized at various temperatures. These images would be very useful for explanation of the phenomenon of "M" shape appeared during TiO_2 thin film photocatalyst degrading the dye solution of Orange II. At lower temperature ranged from 360°C to 430°C the anatase polycrystalline were compactly staked with few amount of porosities, but the crystallite size appeared big and with a coarse surface, especially for 430°C grown sample. This was helpful for increasing the degradation reaction. So the sample of OSA43 (430°C) appeared as one of relative lower shoulder on the "M" shape of photodegradation would be reasonable. From 430°C to 460°C and 500°C the crystallite size shrunk quickly, and the surface roughness decreased correspondingly AFM checked

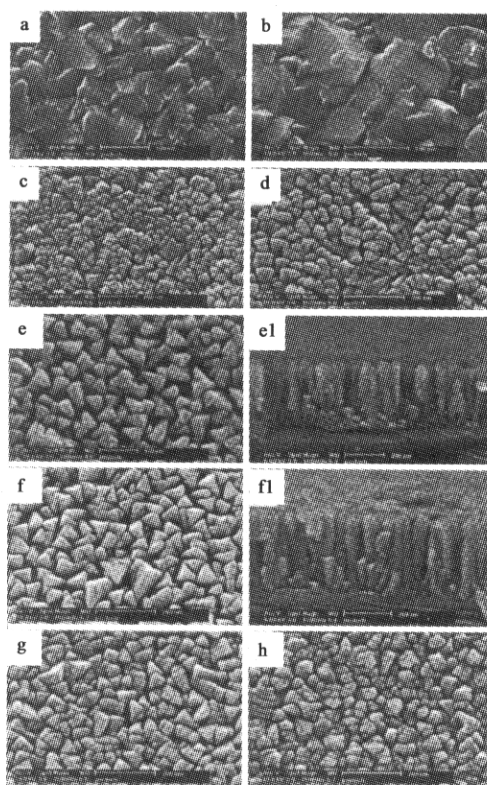


Fig.4 The FE-SEM images of TiO₂ thin films deposited at different temperatures, the top-graph(a), (b), (c), (d), (e), (f), (g), (h) corresponding film deposition temperatures of 360, 430, 460, 500, 600, 700, 800, 900 °C, respectively, (e1), (f1) are the cross-sectional image of 600 °C and 700 °C deposition, respectively

roughness (RAM) of 430 °C, 460 °C and 500 °C films are 16.76 nm, 12.21 nm and 8.41 nm respectively. At this situation the kinetic condition of photodegradation would be deteriorated seriously. The activity of degradation found its lowest position in "M" shape at 500 °C of deposition. As raising temperature to 600 °C, and 700 °C the anatase polycrystalline enlarged again, and formed relative loosely scattered standing arrays (as shown in cross-sectional image of (e1) and (f1)). This loosely heaped columnar microstructure made it possible for liquid solution to penetrate into the vacancy between columns. Therefore it will significantly increase the opportunities of contacting between aqueous solution of dye and solid TiO₂ films. As UV light and solar light can penetrate into TiO₂ film for about 780 nm calculated theoretically in literature (Choi, 2000). So the degradation reaction can carry out even under the surface of film. As a result, the degradation reaction would be significantly enhanced at the condition of 700 °C of film deposition. Thus the activity of TiO₂ film on photodegradation of azo dye displayed the highest position on the shoulder of "M" shape.

Consequently increased deposition temperature to 800 °C and 900 °C particulates of TiO₂ on the surface tended to closely stack one another, and some small particles approached to grow among the vacancy areas between "big" crystallite grains. Meantime the anatase(101) appeared. So

film degradation decreased as shown in Fig.2.

2.2 TiO₂ thin films fabricated within 50 min on Si (100) substrates and illuminated by UV-light

Keeping all of the other TiO₂ film deposition parameters in the same as that of mentioned in Section 2.1 except for changing growth time from 30 min to 50 min, the samples name of MSA36, MSA41, MSA51, MSA61, MSA71, MSA81 and MSA91 corresponded the deposition temperatures of 360 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C respectively. The thickness of as synthesized thin films checked by FE-SEM was in the range of 400–600 nm. The schedules of checking photocatalytic activity were also maintained as that of the last group of experiments. The UV-VIS checked as-illuminated dye solution spectra, relative dye concentration and dye conversion proportion are shown in Fig.5 and Fig.6. The XRD patterns of the as-fabricated thin films are illustrated in Fig.7. The results of degradation tendency were almost the same as that of 200–400 nm TiO₂ thin films. But from 700–900 °C the photoactivities decreasing were not as fast as that of last mentioned group. This may be explained that at the 800 °C and 900 °C, XRD patterns showed a relative high intensity at orientation of (112) for 800 °C and (101) for 900 °C which means the crystallization were better than that of last ones. So it was slowed down the decreasing rate of degradation reaction at high temperature. The influence of films thickness on degradation activity will be elucidating in the next section.

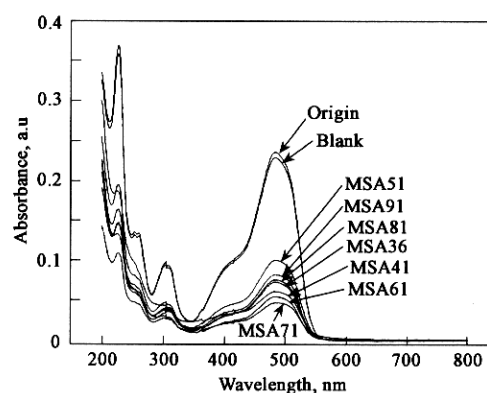


Fig.5 UV-VIS scanning spectra of dye solution photo-degraded by TiO₂ thin films with thickness of 400–600 nm deposited at different temperature

2.3 The comparison of photodegradation activities between different TiO₂ film thickness

The results of proportion conversion of dye achieved by 200–400 (series of OSA), 400–600 (series of MSA), 2000–3000 nm (series of CSA) thickness of TiO₂ film fabricated at various temperature and irradiated 2 h in 6.5 ml 0.01 mmol/L Orange II solution under UV light are shown in Fig.8. Checking this figure, it could be concluded that with TiO₂ films' thickness increasing the activities of photodegradation increased at deposition temperature ranged

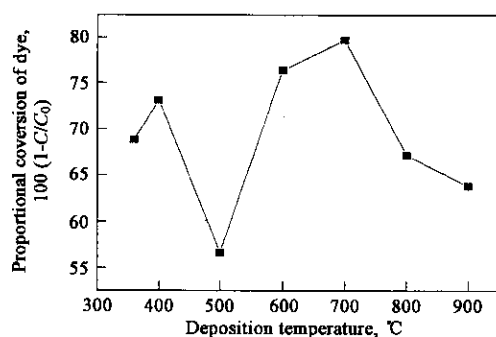


Fig. 6 The influence of TiO₂ thin film depositing temperature on the activity of photo catalytic degradation of dye solution

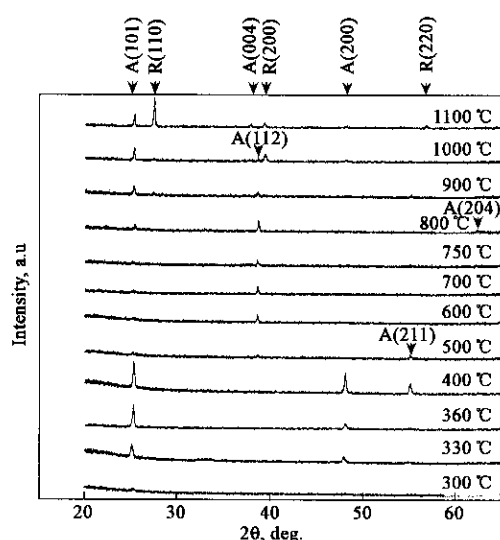


Fig. 7 The XRD patterns of TiO₂ films growing at different temperatures on the substrates of Si(100) within 30 min for each individual deposition

from 500°C to 900°C. It was obvious that almost all of TiO₂ films *in-situ* fabricated (not post-annealing) by MOCVD method displayed a “500°C affect” phenomenon, shown a seriously negative influence on dye degradation activity of TiO₂ film photocatalyst. So it is necessary for future practical operations to avoid manufacturing TiO₂ films around 500°C. Meanwhile for the *in-situ* deposited TiO₂ film on Si(100) substrate also showed a marvelous crystallization phenomenon of “700°C effect”, which would be very useful for improving the degradation ability of TiO₂ films photocatalyst. The “700°C effect” implied that at 700°C deposition, almost one growing orientation of (112) anatase could be gained. This kind of crystallite structure displayed a well standing loosely and regularly scattered nanorod-like parallel columnar microstructure. This kind of microstructure can greatly improve the kinetic reaction condition of degradation at the interfacial area of solid and solution. Therefore it is reasonable to expect for obtaining an improved photo activity of TiO₂ film synthesized by MOCVD system. Here, many experiments with different thickness of TiO₂ films have proved that this expectation is approachable. Some other researchers

such as Bumjoon Kim *et al.* (Kim, 2002) also want to get the (112) orientation dominated crystal structure, and further more to obtain columnar microstructure of TiO₂ film for improving the photoactivity of degradation. They showed that the (112) preferred orientation of TiO₂ films on the substrate of glass fabricated by CVD resulted in better photocatalytic efficiency. But they needed to control the deposition temperature exactly at 360°C, because even 2°C of deviation would cause abruptly decreasing of peak (112) intensity. However, in our experiments, a single anatase (112) has been obtained around 700°C.

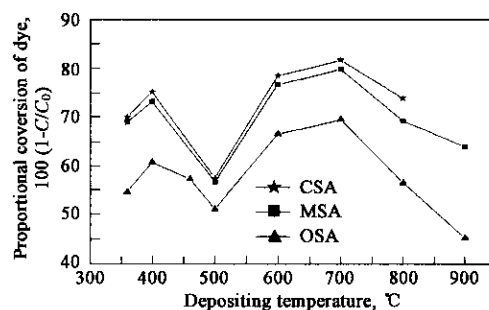


Fig. 8 The relationship between photoactivities and TiO₂ film growth temperatures under three different depositing times

It was obvious that the film thickness changed from 400 nm to 600 nm the film photoactivities increased rapidly, but as the film thickness increased from 600 nm to 3000 nm there was only very small increment could be gained, which should ascribe to that UV light can only penetrated into TiO₂ films to a limited depth (Choi, 2000). So when film thickness exceeds a certain value photocatalytic reaction would not take place anymore. Cui *et al.* (Cui, 1993) also found that thicker TiO₂ film has the higher catalytic activity but at the thickness of 600 nm the activity was saturated. Therefore, a strategy for preparing very thick TiO₂ film is not necessary and essential for the purpose of improving the activity of immobilized TiO₂ photocatalysts.

3 Conclusions

The *in-situ* depositing temperatures of TiO₂ films on silicon(100) substrates have shown that crucial influences on the photodegradation efficiency. The photoactivities varied following a shape of “M”, at lower(360°C), middle(500°C) and higher (800°C) temperatures relative lower photodegradation activities were shown, while deposition at 400°C and 700°C, relative higher efficiencies of photodegradation were demonstrated, especially for that of deposited at 700°C. There appeared “500°C affect” and “700°C effect” tendencies. All of these phenomena should be ascribed to the variation of microstructures at different films synthesized temperatures. Crystallization and single anatase structures (single orientation or poly-orientations) have displayed significant influences on photocatalytic properties.

Films grown at 700°C, one single anatase crystalline orientation of (112), and well-standing loosely scattered columnar structures had been obtained, which resulted in obviously promoting the photodegradation activity of films.

Increasing thickness of TiO₂ films from 200 to 600 nm would significantly enhance the films' photoactivity, but a further thickening TiO₂ film to about 3000 nm showed only relative smaller increment of photodegradation efficiency, that means the photoactivity was saturated at a little more than 600 nm of TiO₂ film.

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Introduction to Material Institute of Northeastern University (NEU) in China

This institute was established about two years ago, the bureau-chief Zuo Liang is the vice-president of NEU. There are 18 professors and among them 13 are Ph.D advisors in the institute. It covers 8 research fields such as crystal-boundary and crystal-tropism, high performance structural materials, functional materials, ceramic materials and organic materials etc. The 1200 m² laboratories have the functions of doing experiments related to material processing and material forming, material mechanics function analyzing, material structural analyzing and material microstructure analyzing (there are one TEM, two SEM with EDX, two XRD *etc.*). Now 8 National High-Tech R&D Projects (863 and 973) of China, and more than 10 projects from enterprises are being carried out in this institute.